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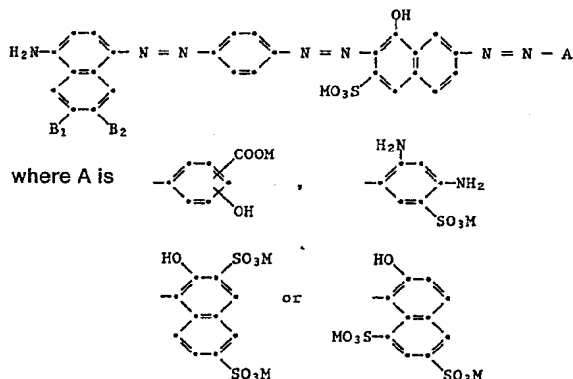
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⑤ **Trisazo black dyes.**

⑤ Black trisazo dyes for cellulosic textiles, leather and especially paper having the structure



one of B₁ and B₂ is hydrogen and the other is -SO₃M or a mixture thereof, and M is hydrogen, sodium, potassium, lithium or -HNR₁R₂R₃ wherein R₁, R₂ and R₃ represent the same or different substituents selected from hydrogen, lower alkyl and lower hydroxyalkyl, and stable liquid concentrates of these dyes are described.

1-15330/= /CGC 1134Trisazo Black Dyes

This invention relates to new trisazo dyes and liquid colorant compositions based on them, to processes for the manufacture of these dyes and liquid colorant compositions and to their use in dyeing and printing materials, particularly paper.

The discovery that some of the intermediates heretofore employed in the manufacture of azo dyes were carcinogenic, such as benzidine, has spurred the search for new azo dyes not based on benzidine. It is therefore an object of this invention to provide new azo dyes prepared without the use of benzidine.

It is a further object of this invention to provide new black dyes particularly suitable for dyeing paper treated with either acid or neutral sizing in deep true shades of pure black or reddish black, with high exhaustion of the dye to the paper and high degree of fastness.

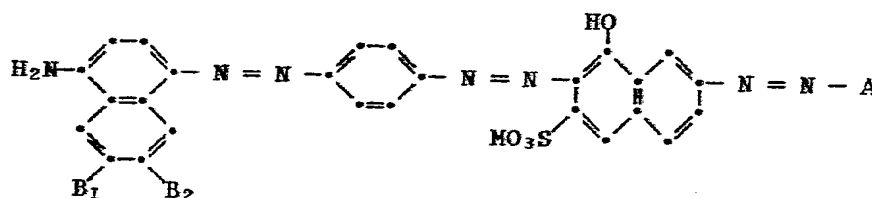
One outstanding advantage of acidic azo dyes is that they may be solubilized with bases to prepare concentrated liquid dyeing compositions. Such liquid formulations eliminate the mess and bother associated with handling dry, often dusty powders. Liquid dye concentrates simplify and speed up the preparation of dyeing solutions since these liquid concentrates can be dispensed either by weight or volume and they disperse immediately. Thus, no time is wasted waiting for the solid dye particles to dissolve.

This latter advantage is particularly important in paper beater dyeing operations where no heating is employed and water temperatures may approach freezing, especially in winter. It is therefore a further object of this invention to provide stable, highly concentrated black liquid dyestuff compositions which can be easily dissolved to prepare stock dye solutions.

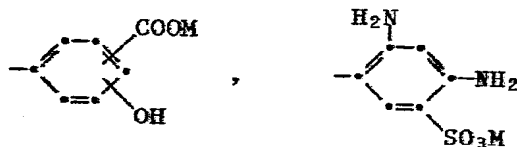
A further advantage of the use of liquid concentrates is decreased dye manufacturing costs since the expensive drying, grinding and standardizing procedures can be eliminated. It is therefore a further object of this invention to provide economical, high strength black liquid colorants for paper.

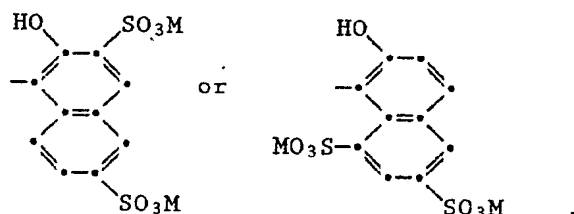
These and other objects of this invention have been achieved with the synthesis of a novel group of trisazo dyes and with the preparation of liquid colorant compositions derived therefrom.

The new compounds are water soluble di-, tri- or tetrasulfonic acid compounds having the general formula:



where A is





In the formula, one of B_1 and B_2 is hydrogen and the other is $-SO_3M$. Mixtures may also be employed. M is hydrogen, sodium, potassium, lithium, or $-HNR_1R_2R_3$ wherein R_1 , R_2 and R_3 are the same or different substituents selected from the group consisting of hydrogen, lower alkyl and lower hydroxyalkyl. Lower alkyl or lower hydroxyalkyl groups are to be understood as meaning those having 1-6 carbon atoms.

The compounds can be prepared by conventional diazotization and coupling reactions from known and readily available starting materials, but these starting materials have not heretofore been combined in the sequence necessary to form the compounds of the general formula. Thus, e.g., p-aminoacetanilide is diazotized and coupled to gamma acid (7-amino-1-naphthol-3-sulfonic acid) under mildly alkaline conditions. Deacylation of the resulting product with alkali liberates the corresponding diamine. This diamine is then tetrazotized and coupled first with one equivalent of 1,6- or 1,7-Cleve's acid or a mixture of the two under acidic conditions. It is then coupled with one equivalent of o-, m-, or p-hydroxybenzoic acid, 2,4-diaminebenzenesulfonic acid, 2-naphthol-3,6-disulfonic acid (R acid) or 2-naphthol-6,8-disulfonic acid (G acid) under mildly alkaline conditions. Alternatively, the diamine intermediate can be subjected to two separate diazotizations and couplings, but this is unnecessarily cumbersome. Accordingly, the former method is preferred.

Following the above procedure usually dyestuff mixtures are obtained containing the trisazo dye of the formula given and the corresponding dye wherein the Cleve's acid and the group A are interchanged.

This invention therefore also relates to dyestuff mixtures obtainable by diazotising and coupling p-amino-acetanilide to 7-amino-1-naphthol-3-sulfonic acid, deacylating the coupling product with alkali, tetrazotizing the resulting diamine and coupling it first with 1,6- or 1,7-Cleve's acid under acidic conditions and then with o-, m- or p-hydroxybenzoic acid, m-phenylenediamine sulfonic acid, R-acid or G-acid under alkaline conditions.

The resulting trisazo dyes can be isolated from solution either in the form of their sodium salts at the end of the final coupling or in the form of the free acid after acidification.

The trisazo dyes are normally prepared initially as the sodium salts for reasons of economy. However, they may also be prepared as the salts of other alkali metals if this is desired for example, to improve solubility. Alternatively, the sodium salt or the free acid form of the dye can be converted into a different salt by known methods. For example, the lithium, potassium, ammonium or alkyl-ammonium salts can be prepared by suspending the dye, in free acid or ion exchange complex form, in water and neutralizing with lithium or potassium hydroxide, ammonium hydroxide, a quaternary ammonium hydroxide or an amine.

Amines which are suitable for use in this invention are preferably C₁-C₈ primary, secondary and tertiary alkyl, alkanol or mixed alkyl-alkanol amines. Such amines include methylamine, ethylamine, propylamine, isopropylamine, n-butylamine, diethylamine, dipropylamine, diisopropylamine, dibutylamine, diisobutylamine methylbutylamine, trimethylamine, triethylamine, diisopropylethylamine, tripropylamine, triisopropylamine, tributylamine, ethanolamine, diethanolamine, triethanolamine, methylethanolamine, dimethylethanolamine, methyldiethanolamine, ethyldiethanolamine, 1-diethyl-

amino-2-propanol and 3-diethylamino-1-propanol. Suitable quaternary ammonium hydroxides include tetramethylammonium hydroxide, tetraethylammonium hydroxide and tetrabutylammonium hydroxide.

Suitable bases for use in the preparation of stable liquid color concentrates are those which substantially increase the solubility of the novel dyes relative to their sodium salts. Preferred bases are lithium hydroxide and secondary and tertiary C₁-C₄ alkanolamines, especially diethanolamine and triethanolamine. Particularly preferred on economic grounds is a commercial mixture containing about 85 % of triethanolamine and 15 % of diethanolamine. If desired, an excess of the base can be advantageously employed to increase the solubility of the dye.

A variety of other substances, all known in the dyestuff art, may be added to either the solid dye or the liquid color concentrates without departing from the spirit of this invention. For example, solid formulations may contain up to 25 % of humectants to prevent drying out during storage, such as sorbitol, glycerine, ethylene glycol, polyethylene glycol, propylene glycol or polypropylene glycol. In liquid color concentrates, such materials, particularly ethylene glycol or propylene glycol and low molecular weight polyethylene glycols, can be used at levels of 5 % to 20 % as freezing point depressants.

Antifoaming agents such as silicones may be added to either the solid or liquid forms of the new dyes. Typically, they are effective at levels of 0.01 % to 2 % by weight.

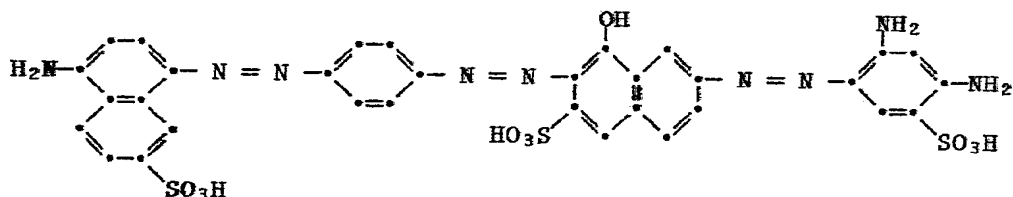
Wetting agents may be added, at levels up to 5 %, to control viscosity and to improve the application of the dyes to the substrate. Typically, wetting agents include dioctyl sodium sulfosuccinate, 2,4,7,9-tetramethyl-5-decyne-4,7-diol and ethylene oxide-ester condensates.

Chelating agents such as sodium hexametaphosphate, tetrasodium pyrophosphate or tetrasodium ethylenediaminetetracetate and hydro-tropic agents such as urea, sodium xylene sulfonate or sodium naphthalene sulfonates can be used, typically at 0.5 to 5 % levels, to improve solubility in hard water.

To prevent mold formation or decomposition by bacteria, antimicrobials and antifungals such as 6-acetoxy-2,4-dimethyl-m-dioxane or sodium pentachlorophenolate may be added in amounts of 0.01 % to about 1 %.

Commercial forms of the new dyes can be either solid or liquid. If solide, they can be in either the free acid form or, preferably, in the form of one or more of the previously described salts. Depending on the additives employed and the drying method, the physical form will vary from fine powders to granules. Spray drying, for example, provides coarse, non-dusting granules.

Because of the excellent solubility of the lithium and alkanolamine salts, stable liquid concentrates containing up to about 25 % dye by weight are readily prepared. Such concentrates are stable, even at elevated temperatures and show excellent freeze-thaw stability. A particularly preferred liquid concentrate is one which contains about 12-22 % by weight of the dye of the formula



and about 14-25 % of an alkanol amine, preferably triethanolamine. It advantageously further contains 10-15 % of a low molecular weight polyethylene glycol and smaller amounts of other previously discussed additives.

Both the solid dyes and the stable liquid formulations of this invention can be used to dye cellulosic textiles and leather. However, they are especially useful for dyeing paper in various shades of black. As paper dyes, they show good all-around efficiency in both acid and neutral sizing and have high affinity and buildup. They can be used alone or in combination with other black dyes for shading purposes. The dye of the general formula wherein A is m-phenylenediaminesulfonate and B₁ is H, for example produces deep black dyeings with a reddish shade. This property can be utilized to advantage to offset the blue or green shades of other black dyes.

The following examples will serve to illustrate the preparation and use of the dyes of this invention. Unless otherwise stated, parts and percentages are by weight and temperatures are in degrees Centigrade.

Example 1: To a stirred slurry of 150 parts of p-aminocetanilide in 240 parts of ice and water at 0°C is added 275 parts of 31.5 % hydrochloric acid. While maintaining 3-5°C with additional ice as needed, 175 parts of a 40 % solution of sodium nitrite is added to the stirred mixture. An excess of nitrite is maintained for at least 15 minutes as indicated by a deep blue color on starch-iodide test paper.

To a slurry of 221 parts of 7-amino-1-naphthol-3-sulfonic acid (gamma acid) in 450 parts of water is added 65 parts of a 50 % sodium hydroxide solution to dissolve the acid and adjust the pH to 6.7-7.3. Then 90 parts of sodium carbonate and sufficient chopped ice to cool the mixture to 0°C are added with good stirring. To this stirred mixture is added, over one hour, at pH 8.4-9.0 and 0-5°C, the diazonium salt mixture prepared above after destroying the excess nitrite with sulfamic acid. Solid sodium carbonate is added as needed to maintain the pH. After completion of the coupling reaction, 7.5 % by volume of solid sodium hydroxide is added and the mixture is stirred for 3-4 hours at 93-95°C to hydrolyze the acetamide group. The mixture is then cooled to 20°C and 2900 parts

of 31.5 % hydrochloric acid are added. At about 3-5°C, the diamine is tetrazotized by adding 330 parts of a 40 % sodium nitrite solution. After maintaining a positive starch-iodide test for one hour, the excess nitrite is destroyed with sulfamic acid and a solution of 172 parts of 1,6-Cleve's acid and 12 parts of 50 % sodium hydroxide in 1000 parts of water at pH 6.9-7.4 is added to the stirred tetrazo mixture at 0-2°C. After addition of about 80-85 % of the Cleve's acid solution, sufficient sodium carbonate solution is added to raise the pH to 2.0-2.5 before completing the addition. This coupling mixture is then added to a stirred mixture of 175 parts of m-phenylenediaminesulfonic acid, 72 parts of 50 % sodium hydroxide, 600 parts of water and 480 parts of powdered sodium carbonate at 5-10°C and pH 8.5-9.6 over 1-2 hours. The coupling mixture is stirred an additional 3-5 hours; then acidified at 83-85°C with 1400 parts of 31.5 % hydrochloric acid to pH 0.5-0.8 to precipitate the black trisazo dye in free acid form. The crude dye is collected by filtration and washed with ice water to remove acid and salt. It is then sucked dry to yield a paste of 22 percent solids.

This dye exhibits a maximum absorption at 570-580 nanometers.

Example 2: At the end of the final coupling and hold period, the dye of Example 1 may be isolated in the form of its sodium salt by vacuum filtration at 5-10°C and pH 8.5-9.0. After washing the cake with 10,000 parts of an 8 % by volume salt solution, sucking dry and drying the product at 95-105°C, there is obtained 920 parts of dry material at 87 % dye strength.

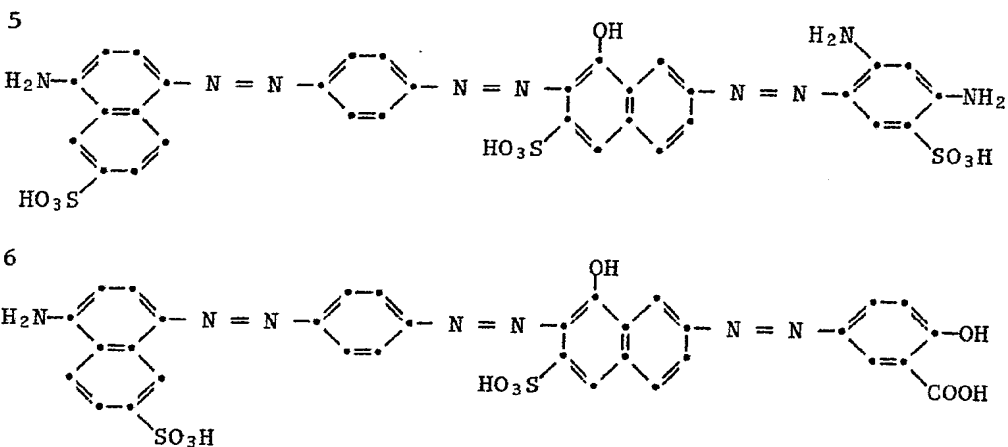
Example 3: A liquid dye concentrate is prepared by solubilizing 100 parts of the filter cake of Example 1 containing 22 parts of dye in a mixture of 45 parts of water, 5 parts of propylene glycol and 23 parts of triethanolamine. The liquid concentrate, which had a dye concentration of 17 %, showed no precipitation after 1 week at 40°C. While precipitation was observed on standing at -10°C, the precipitate redissolved at room temperature.

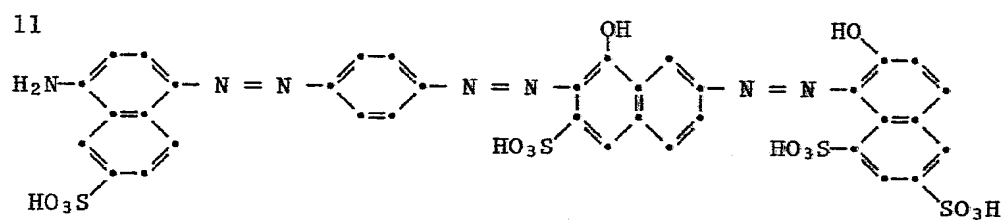
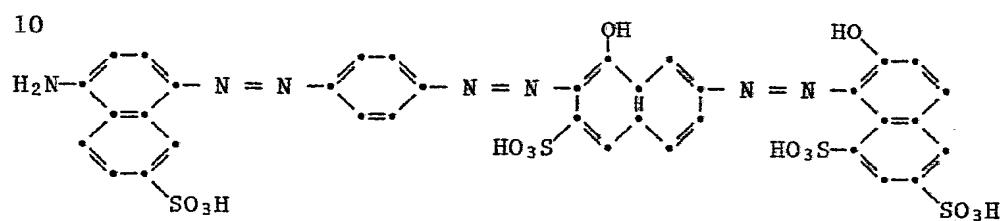
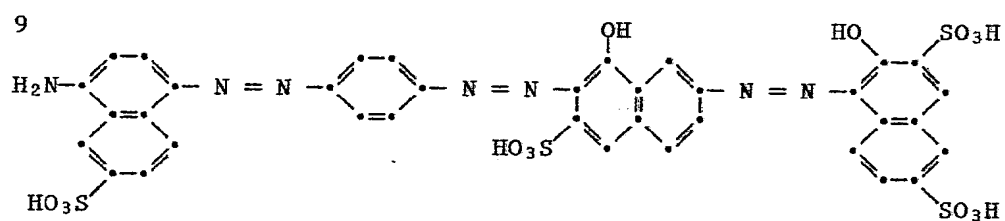
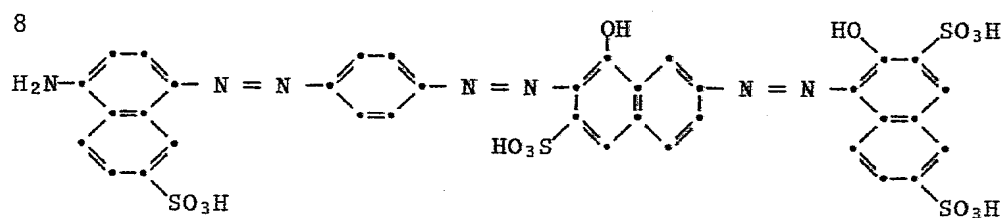
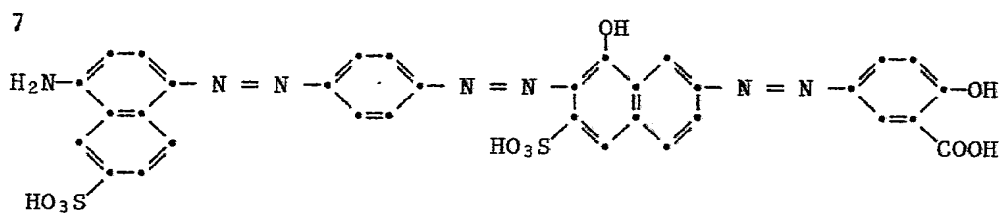
Example 4: To 200 parts of water at room temperature is added 8 parts of 100 % Bleached Softwood Kraft pulp. With vigorous stirring, 10 parts of clay filler and 10 parts of an aqueous 4 % rosin size solution are added. After mixing for 5 minutes, 1.0 part of the concentrate of Example 3 is added and mixing is continued for 10 minutes. The pH is then adjusted to 4.5 with alum. After mixing a further 5 minutes, the pulp slurry is discharged to a sheet mold to form a hand sheet. The hand sheet is pressed between several pieces of blotting paper at 1200 psi and then run through a drum dryer at 350°F.

Neutral sized paper instead of acid sized is prepared by substituting 10 parts of calcium carbonate and 1.0 parts of a 4 % solution of Hercon 48 for the clay and rosin size respectively in the above procedure.

With either procedure, the paper obtained is evenly dyed in a deep reddish black color.

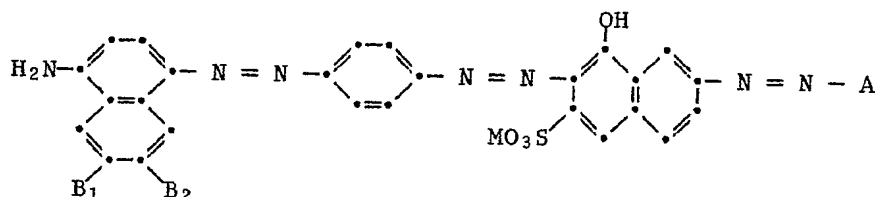
Examples 5-11: The following table shows further dyes which can be produced according to Example 1 using the appropriate terminal coupling components. These dyes can be used for dyeing paper or leather in black shades.



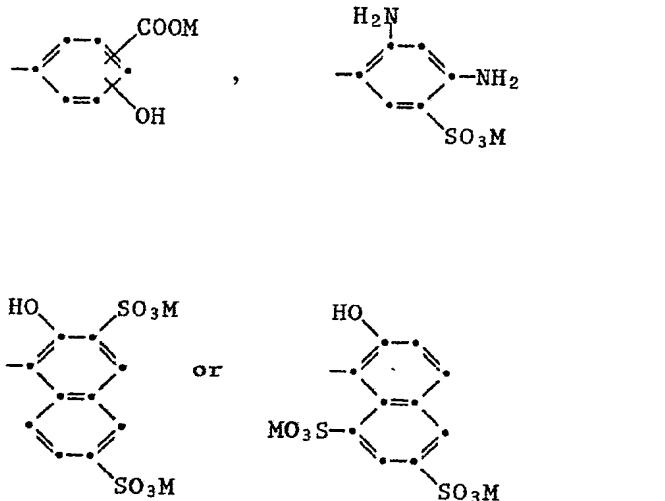


What is claimed is:

1. A compound of the formula



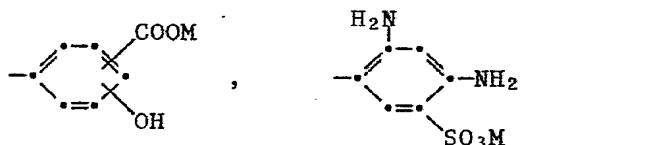
where A is



one of B₁ and B₂ is hydrogen and the other is -SO₃M or a mixture thereof, and

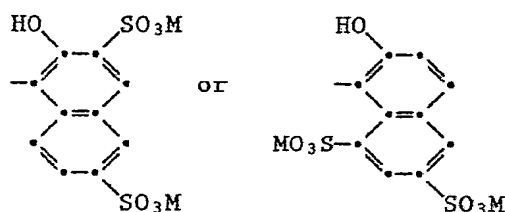
M is hydrogen, sodium, potassium, lithium or HNR₁R₂R₃ wherein R₁, R₂ and R₃ represent the same or different substituents selected from the group consisting of hydrogen, lower alkyl and lower hydroxy-alkyl.

2. A compound of claim 1 wherein A is



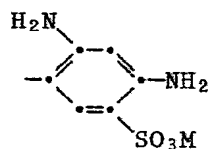
and M is hydrogen, sodium, lithium or -HNR₁R₂R₃.

3. A compound of claim 1 where A is



and M is hydrogen, sodium, lithium or -HNR₁R₂R₃.

4. A compound of claim 1 wherein A is



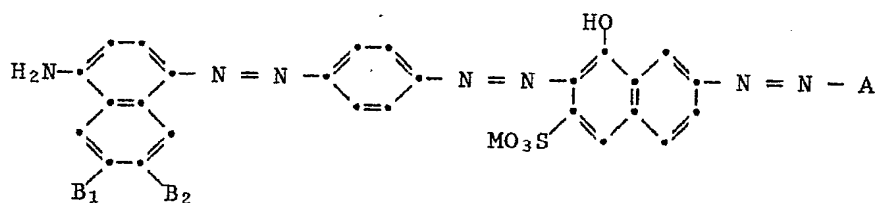
and M is hydrogen, sodium, lithium or HNR₁R₂R₃.

5. A compound of claim 4, wherein B₁ is hydrogen.

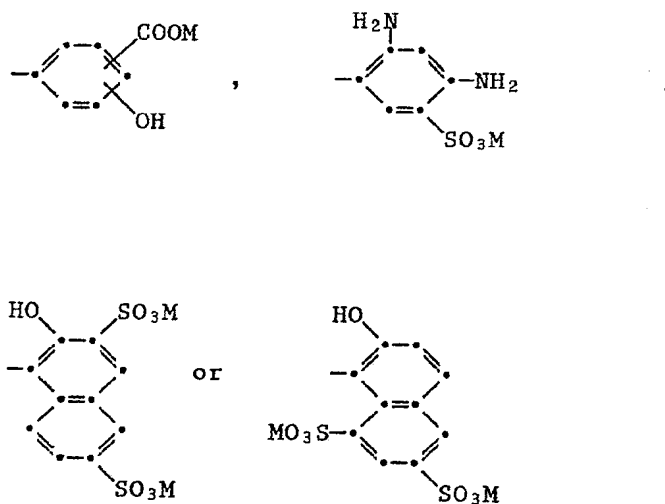
6. A compound of claim 4, wherein B₂ is hydrogen.

7. A compound according to any one of claims 1-4, wherein M is lithium or -HNR₁R₂R₃ wherein R₁, R₂ and R₃ are each lower hydroxy-alkyl.

8. A process for preparing a dye of the formula



where A is



one of B₁ and B₂ is hydrogen and the other is -SO₃M or a mixture thereof, and

M is hydrogen, sodium, potassium, lithium or -HNR₁R₂R₃ wherein R₁, R₂ and R₃ represent the same or different substituents selected from the group consisting of hydrogen, lower alkyl and lower hydroxy-alkyl; comprising the steps of diazotizing and coupling p-amino-acetanilide to 7-amino-1-naphthol-3-sulfonic acid, deacylating the coupling product with alkali, tetrazotizing the resulting diamine and coupling it first with one mole of 1,6- or 1,7-Cleve's acid under acidic conditions and then with one mole of o-, m-, or p-hydroxybenzoic acid, m-phenylenediamine sulfonic acid, R-acid or G-acid under alkaline conditions.

9. A process of claim 8 comprising the further step of acidifying the salt of the dye with a mineral acid after completion of the final coupling reaction.
10. A liquid colorant composition which comprises water, 5-25 % of a dye of the formula of claim 1 wherein M is hydrogen, and from 5-30 % of an amine of the formula $NR_1R_2R_3$ wherein R_1 is hydrogen or lower alkanol, R_2 and R_3 are each lower alkanol, and the amount of amine is at least sufficient to neutralize all the acidic groups of the dye.
11. A liquid colorant composition of claim 10 containing 12-25 % of dye, and 10-30 % of amine.
12. A liquid colorant composition of claim 10 wherein the amine is triethanolamine or diethanolamine or a mixture thereof.
13. A liquid colorant composition of claim 12 containing 12-25 % of the dye and 10-30 % of the amine.
14. A liquid colorant composition of claim 10 which further contains an effective amount of at least one of a humectant, an antifoaming agent, a wetting agent, an anti-sedimentation agent, a chelating agent, an antimicrobial and an anti-fungal agent.
15. A liquid colorant composition which comprises water, 10-25 % of a dye of the formula of claim 1 wherein M is hydrogen and sufficient lithium hydroxide to both neutralize all of the acidic groups of the dye and to effect solution of said dye.
16. A process for the preparation of a liquid colorant composition which comprises the step of mixing a dye of the formula of claim 1 wherein M is hydrogen with water and an amine of the formula $NR_1R_2R_3$ wherein R_1 is hydrogen or lower alkanol and R_2 and R_3 are lower alkanol at 15 to 75°C until a homogenous composition is obtained.

17. A method of dyeing paper which comprises the step of applying to paper fibers or wood pulp, from an aqueous solution, a dye of the formula of claim 1.

18. A method of dyeing leather which comprises the step of applying to leather, from an aqueous solution, a dye of the formula of claim 1.

19. Paper or leather which has been dyed with an aqueous solution of a dye of the formula of claim 1.

20. Dyestuff mixtures containing the dye of claim 1, which mixtures are obtainable by diazotising and coupling p-amino-acetanilide to 7-amino-1-naphthol-3-sulfonic acid, deacylating the coupling product with alkali, tetrazotizing the resulting diamine and coupling it first with 1,6- or 1,7-Cleve's acid under acidic conditions and then with o-, m- or p-hydroxybenzoic acid, m-phenylenediamine sulfonic acid, R-acid or G-acid under alkaline conditions.